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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : A62D	A2	(11) International Publication Number: WO 00/45896 (43) International Publication Date: 10 August 2000 (10.08.00)
(21) International Application Number: PCT/US00/01391 (22) International Filing Date: 20 January 2000 (20.01.00) (30) Priority Data: 09/235,969 22 January 1999 (22.01.99) US (71) Applicant: NORTHROP GRUMMAN CORPORATION [US/US]; 1840 Century Park East, Los Angeles, CA 90067-2199 (US). (72) Inventors: DIMARZIO, Donald; 14 Concord Drive, Northport, NY 11768 (US). PIRICH, Ronald, G.; 14 Charles Circle, Islip, NY 11751 (US). KLEIN, John, F.; 51 Madison Park Gardens, Port Washington, NY 11050 (US). (74) Agents: ANDERSON, Terry, J.; Northrop Grumman Corpora- tion, 1840 Century Park East, Los Angeles, CA 90067-2199 (US) et al.		(81) Designated States: AU, JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: METHOD FOR PRODUCING A SELF DECONTAMINATING SURFACE (57) Abstract <p>A method for producing a self decontaminating surface to decontaminate chemical and biological contaminants that are deposited on the surface and decontaminatable through reaction with free hydroxyl radicals. The method first includes determination of a surface to be treated and which is exposable to ultraviolet light. Second, a coating of nanoparticles of a transition metal oxide, non-limitedly exemplified by anatase titanium dioxide, is applied to the chosen surface. Application of the coating is accomplished by spraying heated nanoparticles or clusters thereof from a feed stock onto the surface to form a nanoparticle coating, with the nanoparticles being at a temperature of at least about 750 °C upon exit from a spray apparatus and of a size between about 5 nm and 100 nm. Finally, the treated surface is exposed to ultraviolet light and water moisture, either naturally from the environment or artificially, to thereby catalytically form free hydroxyl radicals that thereafter react with the contaminants to render them generally harmless.</p> <div data-bbox="841 1150 1369 1906"><pre>graph TD; A[TiO2 CLUSTER FEED + ARGON FEED] --> B[RF INDUCTION PLASMA SPRAY GUN]; B --> C[PLASMA/HEAT GENERATION]; C --> D[TiO2 CLUSTERS APPLIED BY SPRAY]; D --> E[CLUSTER IMPACT ON SURFACE]; E --> F[FORMATION OF NANOPARTICLE COATING]; F --> G[INTRODUCTION OF MOISTURE + UV LIGHT];</pre></div>		

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METHOD FOR PRODUCING A SELF DECONTAMINATING SURFACEField of the Invention

The present invention relates to the treatment of
5 hazardous contamination in general, and in particular to
thermal-spray surface-deposition methodology for the
production of a self-decontaminating photocatalytic
surface capable of neutralizing hazardous organic
chemicals and biologicals through reaction with hydroxyl
10 radicals produced from the interaction of a transition
metal oxide and water in the presence of ultraviolet
light.

Background of the Invention

15 Contamination of exposed structural surfaces with
dangerous chemical or biological material creates a
critical threat in both civilian and military contexts.
In the former context, such civilian contamination can
occur accidentally, such as during the conveyance of
20 hazardous materials from one site to another, or the
civilian contamination can occur on purpose, such as
where a community becomes the target of hostility. In
the military context, chemical and/or biological warfare
can, for instance, occur under test conditions, or it can
25 be present as an actual peril during active conflict. In
any event, such deployed materials can remain for a
significant period of time (e.g. up to several weeks) on
exposed surfaces such as vehicles, aircraft, buildings,
equipment, etc., and thereby remain as dangers to humans
30 and animals that may come in contact with these surfaces
before decontamination is undertaken.

One present decontamination procedure includes the
application of cleaning agents generally coupled with
actual scrubbing of surfaces. Because of the nature of
35 the contaminants, extreme care must be taken to make
certain that any water supply systems, as well as
fisheries, domestic and wild animal water sources, and

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the like, do not become infiltrated because contaminated cleaning agents are rinsed into the sewer system or ground and eventually return in supposedly fresh water for subsequent consumption. A second present
5 decontamination procedure is the application of a fixed coating of titanium dioxide nanoparticles on an exposed surface for subsequent decontamination through ultraviolet catalytic generation of hydroxyl radicals. However, and while such a coating is effective in
10 achieving decontamination, its universality of application under present methodology is severely limited because coating procedures presently taught do not result in efficient, uniform, and rapid particulate deposition.

Thus, in view of the criticality of adequate care
15 and the danger present in exercising that care when dealing with hazardous chemicals and biologicals, it is apparent that a need is present for methodology that can accomplish decontamination of these hazardous substances without severe interference with normal societal
20 activities. Accordingly, a primary object of the present invention is to provide methodology for creating a self decontaminating surface whereby a transition metal oxide can be efficiently and relatively widely deposited on a surface for subsequent reaction with water and catalytic
25 ultraviolet light to yield hydroxyl radicals for decontaminating reaction with untoward contaminants.

Another object of the present invention is to provide deposition methodology that employs a thermal spray technique for coating transition metal oxide on a
30 surface for subsequent decontamination.

Yet another object of the present invention is to provide deposition methodology for nanoparticle cluster impact of the transition metal oxide on the surface whereby the clusters break apart on impact to cause
35 particle dispersion and adherence at the surface interface.

These and other objects of the present invention will become apparent throughout the description of the invention which now follows.

5

Summary of the Invention

The present invention is a method for producing a self decontaminating surface to decontaminate chemical and biological contaminants that are decontaminatable through reaction with free hydroxyl radicals and that are deposited on the surface. The method first includes the determination of a surface to be treated and which is disposed to be exposable to ultraviolet light. Second, a coating of nanoparticles of a transition metal oxide, non-limitedly exemplified by anatase titanium dioxide, is applied to the chosen surface. Application of the coating is accomplished by spraying heated nanoparticles of the transition metal oxide from a feed stock onto the surface to form a nanoparticle coating, with the nanoparticles being at a temperature of at least about 750°C upon exit from a spray apparatus and of a size between about 5 nm and 100 nm. Finally, the treated surface is exposed to ultraviolet light and water moisture to thereby catalytically form free hydroxyl radicals that thereafter react with the contaminants to render them generally harmless.

Generally, any surface can be established as a self decontaminating surface, and can include building structures, ships, aircraft, etc. such as those that may be involved in military operations where hazardous chemicals (e.g. solvents, nerve gases) and/or biologicals (e.g. bacteria, viruses) are potentially involved. A usual source of ultraviolet light is from sunlight, while a usual source of moisture is from ambient humidity. One non-limiting method for applying a nanoparticle coating is spraying a plurality of nanoparticle clusters onto the surface. These sprayed clusters strike the surface and immediately break apart to thereby provide relatively

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uniform nanoparticle surface coverage. Reaction between metal oxide molecules and water molecules, catalyzed by ultraviolet light, results in the liberation of free hydroxyl radicals available for decontamination reaction with chemical and biological contaminants to thereby render the surface safe. In this manner, exposed structural surfaces can be rapidly converted to self decontaminating surfaces that render innocuous the untoward chemical and biological precipitates there deposited.

Brief Description of the Drawings

An illustrative and presently preferred embodiment of the invention is shown in the accompanying drawings in which:

Figure 1 is a block diagram illustrating the treatment of a surface to render the surface self decontaminating.

Detailed Description of the Preferred Embodiment

The present invention provides methodology for rendering a surface self decontaminating with respect to chemical and biological contaminants. Non-limiting exemplary surfaces include building exteriors, ship decks and exposed hull portions, aircraft wings and fuselages, etc. Such self decontaminating is achieved in the presently preferred embodiment, as illustrated in the diagram of Figure 1, by first providing clusters of anatase titanium dioxide nanosized particles in an alcohol suspension. This suspension then is fed into an axial feed RF induction plasma spray gun along with an argon carrier gas. The RF power generates an argon plasma which heats the titanium dioxide clusters to a temperature of about 1,000°C. These heated clusters then are accelerated to velocities from about 100 to 300 meters per second and delivered to the surface to be coated. Upon impacting the surface, cluster break-up

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occurs to thereby uniformly distribute and adhere nanoparticles (e.g. 5 to 50 nm) of titanium dioxide on the surface. A coating of a few (e.g. 5 to 15) micrometers is preferred to thereby be of a sufficient
5 quantity for self decontamination.

As earlier related, in order to achieve surface decontamination properties, the coated titanium dioxide requires two additional components: water moisture and ultraviolet light. Both of these additional components
10 typically are supplied by the environment through ambient humidity and sunlight, respectively. Thus, when a humidity-exposed outdoor surface bearing the coating of titanium dioxide is exposed to natural sunlight, photocatalysis proceeds to produce free hydroxyl (OH)
15 groups capable of reacting with, and thereby decontaminating, untoward chemical and biological contaminants. Of course, when ultraviolet light and/or water moisture sourcing is not available naturally, ambient conditions can be replicated as necessary and
20 practical to thereby artificially produce a self decontaminating surface.

Through implementation of the methodology defined and described herein, a user is able to effectuate a safe environment with respect to surface interactions with
25 personnel who come in contact with such a treated surface during the shelf life of hydroxyl radicals associated with that surface. Thus, while an illustrative and presently preferred embodiment of the invention has been described in detail herein, it is to be understood that
30 the inventive concepts may be otherwise variously embodied and employed and that the appended claims are intended to be construed to include such variations except insofar as limited by the prior art.

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WHAT IS CLAIMED IS:

1. A method for producing a self decontaminating surface to decontaminate chemical and biological contaminants so decontaminatable through reaction with free hydroxyl radicals and deposited on said surface, the method comprising:
 - a) identifying a surface exposable to ultraviolet light;
 - b) spraying heated nanoparticles of a transition metal oxide from a feed stock onto said surface to form a nanoparticle coating, said nanoparticles being at a temperature of at least about 750°C and of a size between about 5 nm and 100 nm; and
 - c) exposing the surface to water moisture and ultraviolet light to thereby liberate free hydroxyl radicals on said surface to react with and decontaminate said contaminants.
2. A method for producing a self decontaminating surface as claimed in Claim 1 wherein said heated nanoparticles are generally molten and splat and solidify on said surface to provide a nanoparticle coating thereon.
3. A method for producing a self decontaminating surface as claimed in Claim 1 wherein said heated nanoparticles are sprayed as a plurality of nanoparticle clusters onto said surface at a velocity sufficient to break apart upon impact with said surface to provide a nanoparticle coating thereon.
4. A method for producing a self decontaminating surface as claimed in Claim 1 wherein said water moisture is provided by ambient humidity and said ultraviolet light is provided by sunlight.
5. A method for producing a self decontaminating surface to decontaminate chemical and biological contaminants so decontaminatable through reaction with

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free hydroxyl radicals and deposited on said surface, the method comprising:

- a) identifying a surface exposable to ultraviolet light;
 - 5 b) spraying heated nanoparticles of anatase titanium dioxide from a feed stock onto said surface to form a nanoparticle coating, said nanoparticles being at a temperature of at least about 750°C and of a size between about 5 nm and 100 nm; and
 - 10 c) exposing the surface to water moisture and ultraviolet light to thereby liberate free hydroxyl radicals on said surface to react with and decontaminate said contaminants.
6. A method for producing a self decontaminating
- 15 surface as claimed in Claim 5 wherein said heated nanoparticles are generally molten and splat and solidify on said surface to provide a nanoparticle coating thereon.
7. A method for producing a self decontaminating
- 20 surface as claimed in Claim 5 wherein said heated nanoparticles are sprayed as a plurality of nanoparticle clusters onto said surface at a velocity sufficient to break apart upon impact with said surface to provide a nanoparticle coating thereon.
8. A method for producing a self decontaminating
- 25 surface as claimed in Claim 5 wherein said water moisture is provided by ambient humidity and said ultraviolet light is provided by sunlight.

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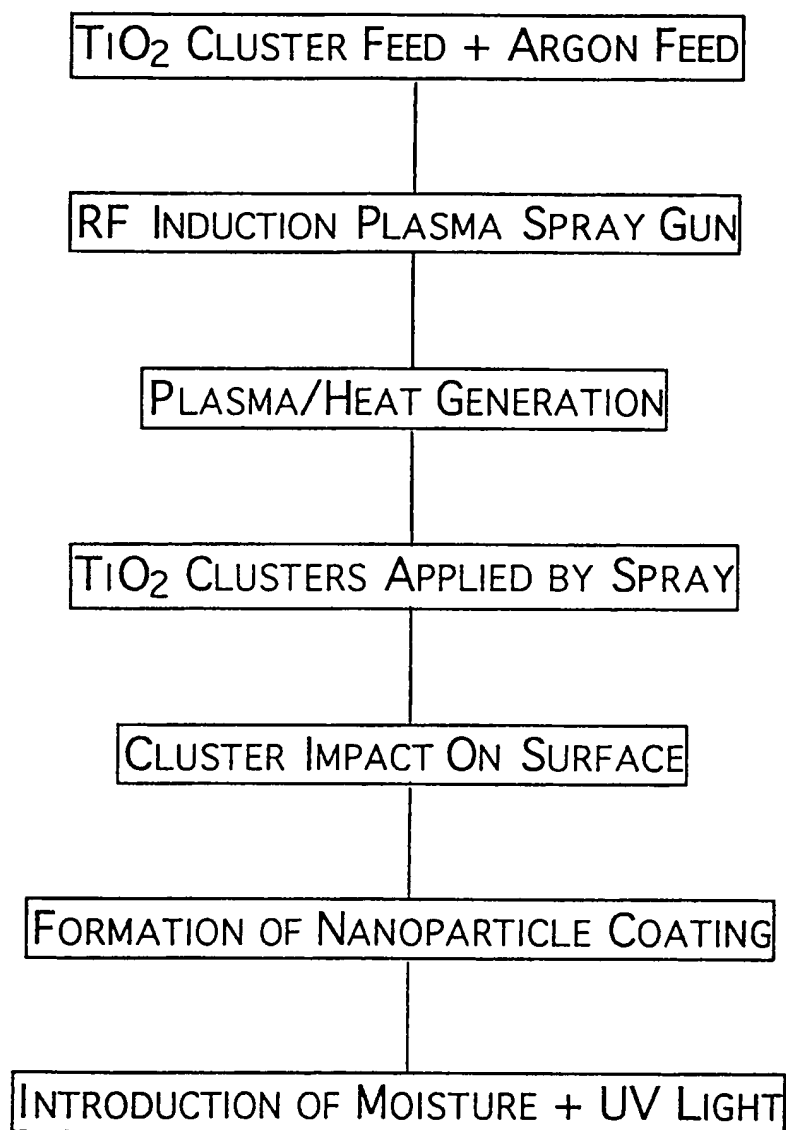


FIGURE 1

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